

*Report on the Separation of Ionium and Actinium from Certain Residues and on the Production of Helium by Ionium.**

By B. B. BOLTWOOD, Ph.D., John Harling Fellow, University of Manchester.

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The material consisted of certain substances separated from 500 kilos. of pitchblende residues purchased by the Royal Society from the Vienna Academy of Sciences, and treated at the works of the Armet de Lisle at Nogent-sur-Marne, in France, for the removal of the radium contained in them. The operations to be described were carried out with that portion of the residual material returned to the Royal Society as "actinium residues." The material consisted of a wet paste, and was a heterogeneous mixture containing considerable proportions of lead chloride and gelatinous silica and small proportions of copper, zinc, iron, tin, and other elements.

* *Note by Prof. E. Rutherford, F.R.S.*—In 1907 the Royal Society kindly allowed me to test the actinium residues in their possession. Preliminary observations on a small fraction of the dried residue showed that it gave off the actinium emanation freely, and contained a small quantity of radium. Observations on the rate of growth of radium in the part of the residue obtained in solution showed that the amount of ionium present was less than 1/10 of the amount to be expected if all the ionium in the uranium residues had been separated with the actinium. This is borne out by the result of the chemical separation of the ionium, which is described in the paper. This result was disappointing, and indicates that the greater part of the ionium was lost in some part of the process to which the main pitchblende residues had been subjected. As there was no definite published information as to the best method of separation of actinium and ionium from such residues, it was necessary to devise suitable methods. Preliminary observations in this direction were made by Dr. Ritzel, a research student in the laboratory. These were continued by Mr. Greenwood, who carefully examined the activity in the form of thin films of definite small fractions of the material obtained at each stage of the chemical treatment. Working on a small scale, a satisfactory method was found of separating the greater part of actinium and ionium from the residues. As the laboratory had no provision for chemical work on the comparatively large scale required, it was arranged that the initial work of concentration should be done by Messrs. Tyrer and Co. at their works, under the direction of Mr. Greenwood. It will be seen that the method applied on the large scale was successful in the separation of the ionium, but did not effect a separation of the actinium at the right point. As activity measurements had been made at each stage of the chemical process it was finally not difficult to locate the position of the actinium, and to affect its partial concentration.

My thanks are due to Mr. Greenwood for his assistance in the initial work of separation, and particularly to Dr. Boltwood for the great trouble he has taken in separating and concentrating the ionium and actinium in the residues.

The preliminary treatment was carried out at the works of Thomas Tyrer and Co., at Stratford, London, under the direction of Mr. H. C. Greenwood, M.Sc., of this laboratory, and consisted of the following operations:—

The weight of the wet paste was 21·2 kilos. The ignition of a small sample indicated that the proportion of volatile material present was equal to 68 per cent. of the total. The paste was heated with 35 litres of commercial hydrochloric acid, the mixture was boiled down to remove the excess of hydrochloric acid, and the residue was boiled with 100 litres of water. The undissolved materials were allowed to subside, the clear solution was decanted, and the remaining solids were repeatedly treated with hot water until all soluble substances had been removed. The insoluble portion was again treated with hydrochloric acid and with water. The solutions obtained were combined and allowed to cool, when a considerable quantity of lead chloride separated. This was removed, and the solution was treated with an excess of hydrogen sulphide. The precipitated sulphides were filtered off, and the solution, after the addition of about 8 litres of strong nitric acid, was heated to boiling. An excess of ammonia was added to this solution, and the mixture was boiled with steam. After standing over night the precipitated hydroxides were removed by filtration, and the filtrate was evaporated down until a considerable residue of ammonium salts was obtained. This residue will be referred to later as *residue B*. The precipitate of hydroxides was dissolved by warming with dilute hydrochloric acid, and the solution was diluted with water. To this solution was added a solution of 3 kilos. of oxalic acid. Ammonia was also added to neutralise the excess of hydrochloric acid. The mixture was allowed to stand for 17 hours, and the precipitated oxalates were filtered off, dried, and ignited at a low red heat. The oxides obtained in this manner were digested with hydrochloric acid, in which they were almost completely dissolved, and the insoluble material was removed from the solution by filtration. This filtrate, after diluting with water to a total volume of about 20 litres, was nearly neutralised with ammonia, and was then mixed with about 20 litres of a 6-per-cent. solution of hydrogen peroxide. The mixture was allowed to stand over night, and the precipitate which formed was filtered off and dried at 120°. The weight of the dried material was 160 grammes.

All of the materials separated in the course of these operations were carefully preserved. The various solutions obtained were concentrated by evaporation. The activities of the different products were measured immediately after they had been separated, and were further observed at frequent intervals over a period of about nine months.

The various operations described up to this point were all carried out either by, or under the direction of, Prof. Rutherford and Mr. Greenwood. The first material placed at my disposal consisted of the precipitate obtained with hydrogen peroxide. As already stated, this precipitate, when dried, weighed 160 grm. Its activity was about 20 per cent. of the total activity of all the substances which had been separated from the original material. An examination of the records of the different measurements which had been made of the activity of this material from the time of its separation showed that the activity had at first risen by about 20 per cent. and had then fallen to about 65 per cent. of its initial value, after which it had remained approximately constant.

A preliminary chemical examination of the precipitate indicated that it contained a considerable proportion of rare earths and calcium, but the somewhat surprising observation was made that very considerable amounts of fluorine were also present. It was at first difficult to account for the presence of this element, but from inquiries it was learned that the hydrogen peroxide solution used for the precipitation had been prepared by a process which resulted in its being largely contaminated with hydrofluosilicic acid. Owing to the presence of the fluorine, the decomposition of the precipitate was extremely difficult, but was finally accomplished by heating the material with concentrated sulphuric acid.

The product obtained in this way was extracted with cold water, and the insoluble portions were again heated with sulphuric acid. After this operation had been repeated several times, a solution containing the rare earths, and an inactive residue consisting of calcium sulphate and silica, were obtained. The solution was heated to boiling and an excess of ammonium oxalate was added. The mixture was allowed to stand for 24 hours and the precipitate formed was removed by filtration. This precipitate was dried and converted into the oxides by gentle ignition. The weight of the oxides, which consisted chiefly of cerium and didymium oxides, was about 95 gm. The oxides were dissolved by hydrochloric acid and the rare earths present were precipitated as hydroxides by adding an excess of ammonia. The hydroxides were dissolved in a slight excess of hydrochloric acid. The solution was diluted, heated to boiling, and an excess of sodium thiosulphate was added. The mixture was boiled for some time, and the precipitate which formed was finally filtered off. This precipitate was decomposed by warming with a slight excess of hydrochloric acid, and the precipitation with sodium thiosulphate was repeated. This operation was carried out in all four times, and the precipitate obtained in the last operation was dried and strongly ignited.

The final material obtained in this manner consisted of pure white thorium oxide and weighed 1.8 gm. It was highly radioactive, because of the ionium which it contained, and had an activity about 3000 times that of an equal weight of uranium oxide. Two thin films of this material, one weighing 1.27 mgrm. and the other weighing 0.65 mgrm., were prepared and the number of α -particles emitted by these films were kindly counted for me by Dr. Geiger. According to his measurements, the average number of α -particles emitted by the total quantity of 1.8 gm. of material was 18.1×10^7 α -particles per second. It has been shown by Rutherford and Geiger* that the number of α -particles emitted by 1 gm. of radium is 3.4×10^{10} per second. The

* 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 162.

amount of ionium present with the thorium was therefore equal to the amount in equilibrium with 5.3 mgrm. of radium.

A sample of the original "actinium residues" had been tested and found to contain a considerable proportion of actinium, but very little actinium, if any, had been separated with the "hydrogen peroxide" precipitate which contained the ionium. An effort was therefore made to discover what had become of the actinium. It has been noticed by several observers* that the precipitation of actinium by ammonia is very uncertain and is often quite incomplete. It therefore appeared highly probable that the actinium present in the original "actinium residues" had remained in solution after the treatment with ammonia described on p. 78. The residue of ammonium salts (denoted on p. 78 and below as "residue B") obtained by concentrating the filtrate from the hydroxides precipitated with ammonia was carefully examined. It was found from the records kept that the activity of these salts had at first fallen to about 70 per cent. of its initial value, and had then risen until it was 20 per cent. greater than when the salt was first prepared. This rise in the activity during a period of about six months indicated the presence of some permanent radioactive constituent having chemical properties similar to those of actinium.

The total weight of "residue B" was about eighteen kilogrammes, and, as already stated, it consisted chiefly of chloride and nitrate of ammonium. By fractional recrystallisation the greater proportion of the ammonium salts were separated and were found to be practically free from radioactive constituents. The ammonium salts remaining in the mother liquor were destroyed by continued boiling with a mixture of hydrochloric and nitric acids. The excess of acid was largely removed by evaporation and the residue, consisting chiefly of calcium salts, was dissolved in water and diluted to a volume of about ten litres. This solution was heated to boiling, and a very slight excess of pure ammonium hydroxide was added. A slight precipitate formed and, when the solution had cooled, this was filtered off. It was finally ignited, and weighed about ten grammes.

The material obtained in this manner was only slightly radioactive when first prepared, but its activity increased rapidly and at a rate corresponding to the recovery of activity by an actinium preparation from which the radio-actinium and actinium X have been separated. After about four months its activity was over 20,000 times that of an equal weight of uranium oxide, and it gave off relatively large quantities of actinium emanation. The relative amount of actinium present in this material was

* Hahn, 'Phil. Mag.,' 1907, vol. 13, p. 165; Levin, 'Phys. Zeit.,' 1907, vol. 8, p. 129; Boltwood, 'Am. Journ. Sci.,' 1908, vol. 25, p. 292.

not accurately determined, but it was roughly estimated to be equivalent to the amount of actinium in equilibrium with 30 mgrm. of radium in a radioactive mineral. A further concentration of the actinium of this material was not attempted.

Production of Helium by Ionium.

A portion of the thorium oxide containing ionium, which was obtained in the chemical operations previously described, was used for determining the production of helium by ionium. The amount of material taken weighed 1.5 gm. This was sealed up with a small quantity of pure oxygen in a tube of Jena "combustion" glass. After a period of 125 days the ionium preparation was heated to a bright red heat, and the gases were pumped out of the tube and collected. The amount of helium present in the gases was then accurately measured, and was found to be 0.031 cu. mm.* The identity of the helium was readily demonstrated by spectroscopic tests.

The number of α -particles emitted by 1.5 gm. of the ionium preparation was 15.1×10^7 per second. This corresponds to the number of α -particles emitted by 0.0045 gm. of radium. Since the production of helium per gramme of radium is 0.107 cu. mm. per day, the amount of helium produced per day by the ionium should be 4.75×10^{-4} cu. mm. In 125 days the amount would therefore be 0.0595 cu. mm. This is about twice the amount that was actually found, but as no other means than heating was employed for displacing the helium from the solid thorium oxide, the fact that the quantity obtained was smaller than the quantity to be theoretically expected is not in itself significant.

The main result of this investigation was to demonstrate clearly that helium is produced by ionium as well as by other products which emit an α -radiation.

* The method employed and the apparatus used for the determination of the helium will be described elsewhere.